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PROBLEMS AND PERSPECTIVES IN PREPARATION OF CaO REFRACTORY

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The development of new materials and technologies is essential for the intensification of the industrial production. This effort is apparent also in the field of the refractory materials, therefore also dead burned lime (CaO) as a refractory material for steel industry is considered. A low hydration and corrosion resistance are the reasons why the CaO refractory has not been widely applied. Research results achieved recently as well as necessary effort for future research activities are discussed in this paper.

Key words: *CaO refractory, lime, hydration, corrosion, overview, perspective*

Problemi i perspektive u pripremi vatrostalnog materijala CaO. Razvoj novih materijala i tehnike je bitan za intenzifikaciju industrijske proizvodnje. Takvo nastojanje je očito i na polju vatrostalnog materijala, zato se razmatra i mogućnost uporabe vapna kao takvog materijala u proizvodnji čelika. Međutim, (ekstenzivna) hidracija i neotpornost na koroziju su razlozi zbog kojih CaO do sada nije imao širu primjenu kao vatrostalni material.

Ključne riječi: *CaO kao vatrostalni material, vapno, hidracija, korozija, pregled, perspektiva*

INTRODUCTION

The use of sintered CaO as a refractory material is not uncommon. Refractory material based on lime as the lining of the Bessemer converter was applied for the first time in 1875 in order to carry out desulphuring and dephosphoring of the molten pig iron. Due to interaction of the porous burned CaO with the atmospheric moisture during dead time followed by damage and disintegration of this casement wall acquit oneself ill. Later on dephosphoring was carried out in the Thomas converter by means of sintered dolomite. No research and development in this refractory material was improved due to negative experience in its application. Since 50th the research in this field started again and during the following ten years good experimental results were obtained leading to the industrial application of CaO refractoriness in metallurgy. As a result, there were several theoretical and experimental successes coupled with the practical applications in metallurgy [1]. And what about perspectives for this refractory? The CaO is occurring in nature as a relatively pure limestone (CaCO₃). The successful application of this highly refractory CaO material with melting point (about 2600 °C) would bring about economical solution of shortage of other raw materials that may have better refractory properties. Lime is stable in the presence of carbon at

elevated temperatures therefore it is advantageous to use CaO-C mixture as a material with adequate slag resistance. Low vapour pressure of CaO at high temperatures is also an interesting property. This fact seems to be of utmost importance in the vacuum refining of steel - VOD and AOD Vacuum Oxygen Decarburization and Argon Oxygen Decarburization, respectively. From the point of view of the steel quality the ability of CaO to bind non-metallic inclusions from the molten steel is also important [2].

As indicated above, the main problems encountered in the production of CaO refractory are following: low resistance to hydration and corrosion. As a result of this CaO had not been often used in industrial processes. On the other hand, much effort has recently been devoted to solve these problems. It is necessary to prepare CaO refractory for the market as well as for satisfaction of metallurgical applications [2].

This work describes the state-of-the-art and perspectives of industrial applications of CaO as a refractory material with the aim to propose future developments in this field.

THE STATE-OF-THE-ART

Methods of CaO preparation

It follows from the literature survey that there are several methods of CaO preparation, namely:

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- CaO fusion from limestone or hydrated lime or marble;
- grinding of limestone, burning at high temperature (one-stage burning process);
- grinding of limestone, pelletizing and burning at high temperature (one-stage burning process);
- grinding of calcined lime, palletising and burning (two-stage burning process);
- pelletizing of hydrated lime and burning (two-stage burning process) [3];
- slip casting of suspension $\text{Ca}(\text{OH})_2$ with arabic gum or casting of suspension burned CaO with organic solvent (various type alcohols) [4];
- hot - pressing limestone, $\text{Ca}(\text{OH})_2$ or CaO [5].

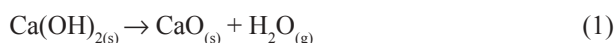
Up to present economically feasible method by which CaO refractory showing good resistance to corrosion and hydration has not been developed. This fact prevents its extensive application in industrial processes. The CaO converter lining in Poland [6] and continuous casting of steel in Liuzhou Iron & Steel Co. (China) [7] for liquid steel filtration and steel vacuum processing (AOD and VOD) in Japan [6, 8] are exceptions. Another possible applications for the CaO refractory is the cement industry.

Casting of calcium hydroxide suspension as a method of preparation of CaO clinker seems to be promising, but there the detailed information about the process is missing.

Two-stage burning process, which consists of the heating to high temperatures (2100 °C), melting in the electric resistance furnace or high-temperature pressing, followed by CaO hydration lowering, but the unfavourable economy of such method of CaO production is the reason why other approaches are still being tested. (for example one-stage burning process of raw material with suitable addition).

CaO hydration

It is known that CaO normally reacts with the atmospheric moisture. This process is responsible for its degradation as it leads to the formation of calcium hydroxide. This reaction is accompanied by increase in volume (198 %) followed by a complete transformation of CaO to $\text{Ca}(\text{OH})_2$ powder. From the kinetic point of view this kind of reaction is solid + gas \rightarrow solid (1), (or solid + liquid \rightarrow solid). According to Schlegel [1], maximum rate of hydration reaction is achieved at 100 °C and at 547 °C the rate drops to zero. Under this condition reaction proceeds then in an opposite direction, i.e. $\text{Ca}(\text{OH})_2$ decomposes.



The process kinetics depend on several factors:

- **the temperature** - as the process controlled by diffusion, its rate depends little on temperature, while process

controlled by chemical reaction depend on the temperature strictly. As a consequence, the diffusion coefficients are linear functions of temperature whereas the rate constants of reactions controlled by chemical reaction are exponential functions of temperature;

- **the pressure** - at constant temperature the velocity of gas molecules hitting the solid surface is proportional to pressure in accordance with the kinetic theory of gases;
- **the sample quality** - the kinetic of solid - gas reactions type is highly affected by quality of interface which can be influenced by these factors: nature and amount of impurities, contents and composition of glass phase, porosity and pore size distribution and also largeness and character of crystals etc. [9]. If the porous material is used, the reacting gas confronts toward lower resistance on the interface. In case if the solid has the spherical shape (or the form of uniform grain size powder, cube, cylinder with the same diameter and height, respectively), the process rate is described by eq. (2):

$$1 - (1 - \alpha)^{1/3} = kt \quad (2)$$

If the solid is compact, the diffusion through reaction product will be the rate controlling step. For reactant in form of sphere the reaction rate will be described by eq. (3) or (4):

$$(1 - (1 - \alpha)^{1/3})^2 = kt \quad (3)$$

$$1 - (2/3) \alpha - (1 - \alpha)^{2/3} = kt \quad (4)$$

where α is conversion, k rate constant and t time, respectively.

The deviation from given equations results from the formation of small cracks, as well as from side reactions [10].

Several experimental investigations were carried out in order to study kinetics of CaO hydration, but the final explanation of the mechanism of CaO hydration has not been proposed. This is the reason why further research in this area is needed.

According to Irabien [11] there are two problems associated with this kind of reaction, namely a) extreme heat development and b) fact, that the volumes of product and reactant are different what causes both of thermal and mechanical stresses in solid material followed by crack development, pores congestion and new porosity formation during the course of reaction. The CaO hydration was described as a very complex heterogeneous reaction running at the solid/gas interface and solid state diffusion. No initial stage of reaction was clarified because of the complexity of both of crack propagation and formation of pores.

Ramachandran [12] studied the CaO hydration by using of dimension and mass changes measurement as well as

porosity distribution. The experiments were carried out at the water presence in the liquid form as well as water moisture (relative vapour pressure 0.5) at the 23 °C. At the water excess the CaO hydration mechanism is predominantly through solution and crystallisation, what permits the crystals creation and growing in the pores and on the original CaO occurrence places. By this method the lowering of pores volume and their size have been achieved. On the other hand if hydration occurs at the solid-vapour interface as a topochemical or solid-state reaction, the product is formed at the original sites of the reactant. As the specific volume of the product is much greater than that of the reactant, the products are pushed from these sites and there is a large over-all expansion. This is in contrast to the diffusion mechanism operating in the liquid water hydration. As a result of an increase of mass with time in the water vapour environment, this phenomenon was suggested as a new method of CaO reactivity determination.

Ritchie [13] observed hydration mechanism of calcined lime (at temperature 920 °C, 10 hours) first by rotation disc method and second as powder sample. In first case the rate of hydration depended on the rate of disc rotation and the controlling step of reaction was diffusion of calcium hydroxide from the reaction interface. In the second case the hydration rate of powdered CaO depended on powder particle size and calcination conditions of limestone. High temperature and long-time calcination decreased hydration rate. In both cases the same reaction mechanism was determined.

Methods used to increase CaO resistance to hydration

It is clear that the hydration depends on the specific area and is joined with porosity and material bulk density. It was shown that by decreasing the specific area of CaO, e.g. by increasing its bulk density by burning, the hydration resistance is increased. The CaO grain size is considered to be another possible factor controlling the hydration rate. It is therefore necessary to obtain good rounded CaO crystals by controlled burning and thus reduce the surface area being accessible to humidity [14].

The stability of CaO grains toward to hydration was solved by adding different inorganic and organic to starting material. Except for several clear cases there is rather big disagreement in the opinion concerning the type and the amount of additives. Moreover, not every study investigated the CaO hydration resistance.

The impurities present in the raw material or studied additions (mostly oxides) cause the lowering of sintering temperatures by creation of compounds having lower melting points in comparison with pure CaO. On the other hand, it can cause the lowering of refractoriness as well as decrease in stability at elevated temperatures. Among additives studied, most favourable (in terms of bulk density and hydration resistance) seem to be Al_2O_3 [15-17], Fe_2O_3

[2], $\text{Ca}(\text{OH})_2$ [16,18]. By adding these materials to either CaCO_3 or CaO high bulk density (90 to 95 % of the theoretical density) and low porosity were reached by one- or two-stage burning. By addition of Al_2O_3 in the oxide form and as chelate compound and Fe_2O_3 (in amount of max. 10 %) also high hydration resistance was obtained. Additions of $\text{Ca}(\text{OH})_2$ and Al_2O_3 had positive effect on lowering of porosity and as well as on CaO grain growth. This one is caused probably by enhancing of process by origination of high reactive CaO from $\text{Ca}(\text{OH})_2$ decomposition when $\text{Ca}(\text{OH})_2$ is used.

The MgO , ZnO , ZrO_2 , SnO_2 , NiO , Cr_2O_3 , V_2O_5 , MnO , Co $\text{Ca}(\text{PO}_3)_2$ additions have no effect on hydration resistance [14].

Another possibility how to hinder CaO hydration is by covering CaO grains by a thin layer of CaCO_3 . This method brings about decrease of the hydration rate in comparison with the case of unprotected CaO particles [19].

Fast hydration of finished CaO can be stopped by addition of suitable hydrophobic liquid for impregnation. Final protection of CaO brick by immersion into PVC or PVC tricresolphosphate emulsion as well as by packing in plastic cover before practical use was described several times [9, 7, 20].

The impregnation and covering of CaO bricks burned at max. 1700 °C by pitch were documented in [15, 21]. This method improved CaO hydration resistance as well as reduced the reaction of refractory lining with slag. However, the significant corrosive resistance was not significant in comparison with dolomite and periclase bricks.

CaO resistance to corrosion

This property has not been studied extensively. Based on comparison with similar dolomite materials it is possible to suggest that following methods may be implemented with the objective to increase the resistance to corrosion [6]:

- increase CaO bulk density (near to theoretical value 3,34 g/cm³);
- presence of the spherical CaO grains, which are able to lower the dissolution in the slag;
- lowering of the phases content, which are created by reaction of dominant compound with impurities. These assist to the chemical penetration of the slag into refractory material,
- impregnation of the CaO material by pitch or other carbon- based substances.

CONCLUSION

On the basis of the published results, dedicated to CaO-based refractory materials it may be concluded that this area needs further investigation. The essential characteristic property - hydration resistance was observed only in few

cases and even in aqueous environment. The absence of exact information about hydration mechanism is evident.

The influence of preparation method of input materials on production of high quality clinker seems to be important. However the references about the optimum conditions of grinding of the initial raw material and about influence of pressure on preparation of clinker are still missing.

The starting raw material, CaCO_3 used in the production of the refractory materials is abundant. It is clear that each material has specific properties therefore it will show different behaviour during the production process. This is the reason why it is necessary for each material to propose individual experimental routine with the aim to determine input material characteristic and their influence on final product properties (hydration and corrosive resistance). Then it would be also useful to make decision about suitable additives to starting material with respect to final properties of CaO refractory. These facts should be taken in account, if we want to prepare high quality refractory material based on lime.

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